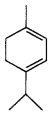
IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet NO3_VOC40

This data sheet last evaluated: June 2013; last change in preferred values: June 2013.



NO_3 + (α-terpinene) → products

Rate coefficient data

k/cm^3 molecule^{-1} s^{-1}	Temp./K	Reference	Technique/Comments
Relative Rate Coefficients			
$(1.82 \pm 0.07) \times 10^{-10}$	294	Atkinson et al., 1985	RR (a)
$(1.03 \pm 0.06) \times 10^{-10}$	298	Berndt et al., 1996	RR (b)

α-terpinene is 1-isopropyl-4-methyl-cyclohexa-1,3-diene.

Comments

(a) 4000 L Teflon chamber at 980 mbar (735 Torr) of air. NO_3 was generated by the thermal decomposition of N_2O_5. Correction made to the α-terpinene loss rate due to reaction with NO_2 was 10 – 47 %. α-terpinene and 2,3-dimethyl-2-butene (reference reactant) were monitored by GC. The rate constant ratio, $k(NO_3$ + α-terpinene) / $k(NO_3$ + 2,3-dimethyl-2-butene) = 3.18 ± 0.13 is placed on an absolute basis by $k(NO_3$ + 2,3-dimethyl-2-butene) = 5.72 × 10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

(b) Flow tube at 15 mbar N_2. NO_3 was generated by the thermal decomposition of N_2O_5. Various detection schemes (electron impact MS, FTIR and GC-MS/FID) were available though it is not stated which was used for the relative rate analysis. The rate constant ratio obtained, $k(NO_3$ + α-terpinene) / $k(NO_3$ + 2,3-dimethyl-2-butene) = 1.796 ± 0.10 is placed on an absolute basis by $k(NO_3$ + 2,3-dimethyl-2-butene) = 5.72 × 10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K (Atkinson and Arey, 2003).

Preferred Values

Parameter	Value	T/K
k /cm^3 molecule^{-1} s^{-1}	1.8 x 10^{-10}	298
Reliability		
Δ log k	± 0.25	298

Comments on Preferred Values

Despite use of the same reference reactant, the two relative rate studies derive rather different rate coefficients. It is not clear whether this is due to the different pressures and bath gases used. The preferred value of the room temperature rate coefficient is based on the relative rate study of Atkinson et al. (1985) in which the experiments were carried out at roughly atmospheric pressure and in air. The error limits are expanded to reflect the poor agreement between the two studies and the necessity to correct for removal of α-terpinene by reaction with NO_2.

The large rate constant and its negative temperature dependence indicate that addition of NO_3 across a double bond to form a nitrooxy- radical is the initial step. Organic nitrates (but not peroxy-nitrates or carbonyls) have been observed in N_2/O_2 bath gas and p-cymene is observed at yields of ~6 % at pressures of N_2 or air above 100 Torr (Berndt et al., 1996).

References

Atkinson, R., Aschmann, S. M., Winer, A. M., and Pitts, J. N., Env. Sci. Tech., 19, 159-163, 1985.

Atkinson, R., and Arey, J., Chem. Rev., 103, 4605-4638, 2003.

Berndt, T., Böge, O., Kind, I., and Rolle, W., Ber. Bunsen-Ges.Phys. Chem. 100, 462-469, 1996.